IV.F.12 Evaluation of Partial Oxidation Fuel Cell Reformer Emissions

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Objectives

- Measure the emissions from a partial oxidation (POx)/autothermal reformer (ATR) fuel processor for a proton exchange membrane fuel cell system under both cold-start and normal operating conditions
- Assess the feasibility of meeting emissions standards for automobiles and light-duty trucks through the use of a fuel cell vehicle with a flexible-fuel reformer

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- K. Emissions and Environmental Issues

Approach

- Define a representative test cycle consisting of both start-up and normal operating conditions
- Use the established test cycle to quantify emissions from a POx reformer before and after anode gas burner (AGB) treatment
- Measure emissions with continuous emissions monitoring (CEM) measurements supplemented with laboratory analyses of speciated hydrocarbons and particulate matter (PM)
- Use reasonable approximations and estimates to convert emissions data from a grams/unit fuel basis to a predicted grams/mile basis

Accomplishments

- Measured emissions from a gasoline-fed fuel processor (without fuel cell) over several operating conditions
- Measured emissions from an ethanol-fed fuel processor with fuel cell over several operating conditions (analysis pending)
- Speciated total hydrocarbon (THC) data before and after the AGB
- Assessed the sensitivity of monitoring equipment over a range of operating conditions
- Analyzed grab sample data to identify correlation between power output and emission levels at transient and steady-state power output levels
- Established testing plan for additional tests based on the data analysis and testing experience of testing two reformer systems

Future Directions

- Continue to analyze existing and future data for correlation trends between power output and emission levels
- Perform extensive emissions testing of a fuel cell/reformer system to include particulates, formaldehyde, and ammonia as well as NO_x, hydrocarbons, and CO
- Sample and analyze emissions from Nuvera Fuel Cells fuel processor-fuel cell system
- Project on-road emissions from fuel cell vehicles with on-board reformers

Introduction

Fuel reformer operation is generally divided into two operating modes: start-up and normal partial oxidation. During start-up, the fuel processor burns fuel at near stoichiometric conditions until critical system temperatures and pressures stabilize to target values. Once the target conditions are reached, the reformer operates in normal mode, in which the fuel processor burns fuel at very rich conditions. Since these modes are comprised of considerably different operating conditions, it follows that the emissions associated with each of these modes are also considerably different.

The combustor is typically cold under start-up conditions, generating emissions during this brief period (target times are under 30 seconds) that can be substantially higher than those produced during the remaining, much longer portion of the driving cycle. The pollutant emissions produced during start-up operation include NO_x, CO, formaldehyde, and organic compounds. These organic compounds, including hydrocarbons, alcohols, and aldehydes, are regulated in California and referred to as non-methane organic gases (NMOG). Under normal, fuel-rich operating conditions, virtually no NO_x is formed, although the formation of ammonia is possible. Most hydrocarbons are converted to carbon dioxide (or methane and/or hydrogen if the reaction is incomplete); however, trace levels of hydrocarbons can pass through the fuel processor and fuel cell. The shift reactors and the preferential oxidation (PrOx) reactor reduce CO in the product gas, with further reduction in the fuel cell. Thus, of the criteria pollutants (NO_x, CO, and hydrocarbons [NMOG]), NO_x and CO levels are generally well below the most aggressive standards. NMOG concentrations, however, can exceed emission goals if these are not efficiently eliminated in the catalytic burner.
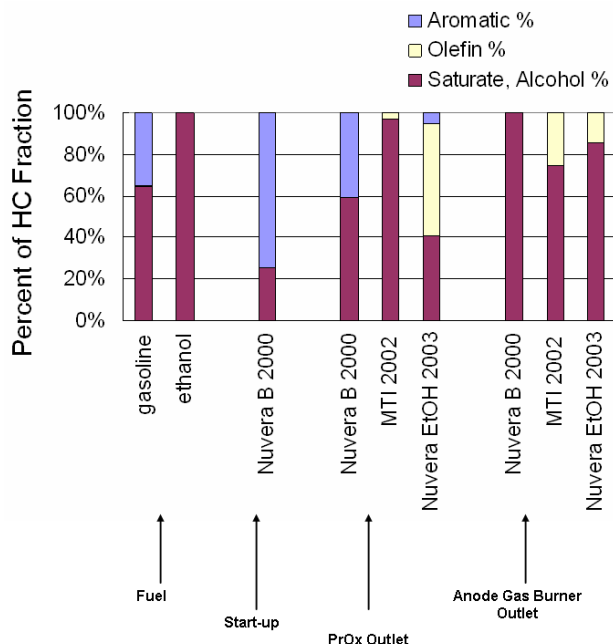
Approach

In this study, a gasoline fuel processor and an ethanol fuel processor were operated under conditions simulating both start-up and normal operation. Emissions were measured before and after the AGB in order to quantify the effectiveness of the burner catalyst in controlling emissions. The emissions sampling system includes CEM for O_2, CO_2, CO, NO_x, and THC. Also, integrated gas samples are collected in evacuated canisters for hydrocarbon speciation analysis via gas chromatograph (GC). This analysis yields the concentrations of the hydrocarbon species required for the California NMOG calculation. The PM concentration in the anode burner exhaust is measured through the placement of a filter in the exhaust stream.

Emissions data will be used to project on-road emissions for fuel cell vehicles with reformers. Emissions data will be characterized in terms of start-up and reforming modes. Although current fuel processor technologies are not configured to follow a typical vehicle load profile, hybrid vehicle power management strategies may facilitate using such fuel processors. For this project, the fuel processor is operated at several steady-state points while emissions are monitored for the steady-state conditions and transients between load changes. The data collected during start-up, different loads, and transients serve as inputs to a vehicle emissions model. Using these data, this vehicle emissions model then predicts the emissions for each second in a driving cycle based on load. Start-up emissions are considered along with the total driving emissions.
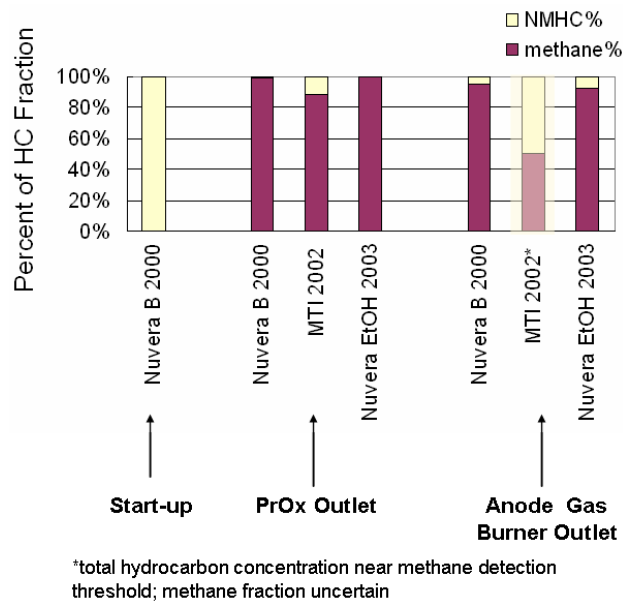
Results

During FY 2004, data from two reformer test sessions were analyzed. The data for each run were

Figure 1. Reformer System Speciation of Non-methane Hydrocarbons

*total hydrocarbon concentration near methane detection threshold; methane fraction uncertain

Figure 2. Reformer System Methane and Non-methane Hydrocarbon Speciation

combined into data sheets, including data taken by TIAX test engineers, reformer output data from the test sites, continuous emission data taken during the test sessions, and GC data. The data from the different sources for each run were systematically matched up for the proper time stamps and categorized in terms of load output and load state (start-up, steady-state, transient). In many cases, at different intended load points, the reformer load data shows the reformer "hunting" around for a steady-state point. This may come from asking the reformer to run under non-optimal conditions. Because of the variable status of the reformer, it is difficult to conclude whether some data sampling points are more representative of steady-state or transient conditions. In an attempt to quantify these impacts, load data output was filtered to several levels and then grouped in order to determine the influence of these fluctuations without a large sample size of steady-state data.

GC data samples were taken at either the PrOx or AGB outlet positions. During each test, continuous emissions sampling was performed at the outlet not sampled by the GC. Speciated total hydrocarbon results were analyzed in detail at the various load output levels and sample points (see Figures 1 and 2).

Trying to analyze the speciated hydrocarbon output emissions (AGB output) proved difficult because many of the species were not present in concentrations above the analyzer detection thresholds, as in the case of the MTI 2002 AGB outlet methane fraction shown in Figure 2. Analysis of data across runs at similar load points was completed to increase sample size, but only two steady-state load points were identified for each set of data, making identification of trends difficult and establishing correlations impracticable. This data does show the high efficiency of the AGB for most HC emissions. Identification of the AGB efficiencies by pollutant across each run, assuming zero for the runs with undetectable levels, could prove to be effective data to move forward with analysis focused on the PrOx output emission levels. This would greatly increase the sample size of data points available for analysis.

New test plans were developed for testing to be completed in the fall of 2004 with previous experiences and analyses in mind. More care will be made to take the optimum running conditions of the reformer in mind, as well as the typical operational procedures. The stability of the load output will be monitored more closely during the runs so that steady-state data samples are the first priority. We

feel that identification of steady-state emissions correlations must first take place before testing the influences of transients.

Conclusions

The combustion of reformer products at the AGB did not represent an optimized fuel cell vehicle configuration. Even with these limitations, the following conclusions can be drawn from the data.

- The AGB was very effective in controlling THC emissions. THC tailpipe emission levels were undetectable in many runs.

- In-use THC and CO emissions were under 0.2 ppm and 3 ppm, respectively, which would correspond to on-road emissions well below the California Super Low Emission Vehicle standards.

- Estimations of start-up on-road NMOG and CO emissions with an optimized fuel processor have been difficult to produce with the small sample size currently available. While this work continues, further tests could prove to be valuable.